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Thermodynamics of Phase Change Solvents

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CCS Conference 2013: 28-29 May, 2013

Antwerp, Belgium

CERE

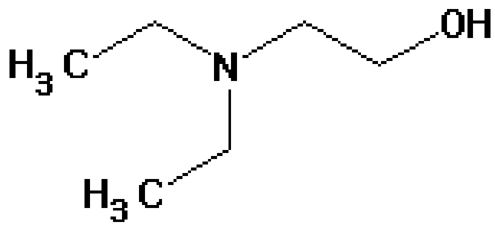
Center for Energy Resources Engineering

Outline

- Introduction
- Experimental Work
  - Freezing Point Depression
  - Heat of Absorption
  - Vapor liquid equillibrium
- Thermodynamic Modeling
  - DEEA-CO_2-H_2O
- Main Conclusions
- Future work

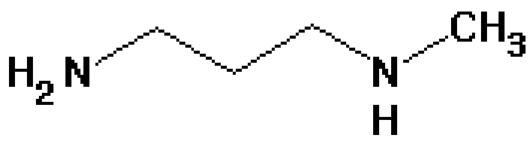
Introduction

2-(diethylamino)ethanol **(DEEA)**



- Low heat of reaction (bicarbonate)
- Low heat requirement for reversion
- High loading capacity
- Low reaction rate

3-(methylamino)propylamine **(MAPA)**



- Fast reaction rate
- High heat of reaction (carbamate)
- High heat requirement for reversion

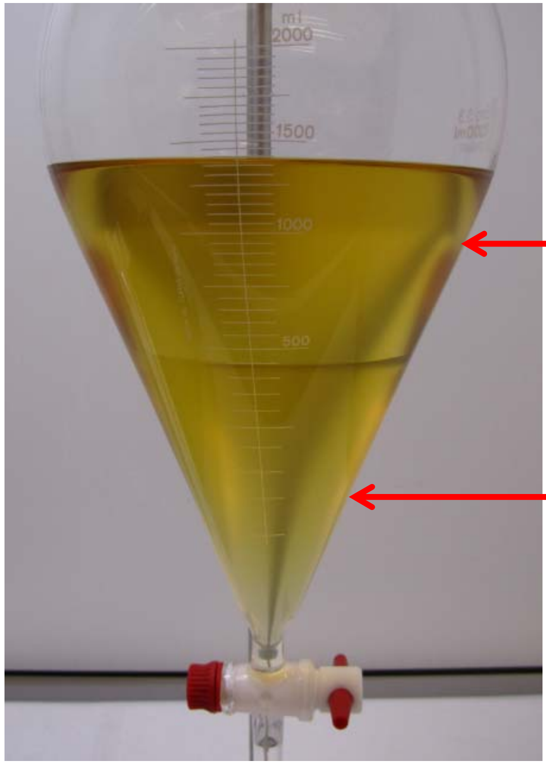
Introduction

DEEA-MAPA-CO_2-H_2O system give liquid-liquid split with lower phase rich in CO_2 and upper phase lean in CO_2

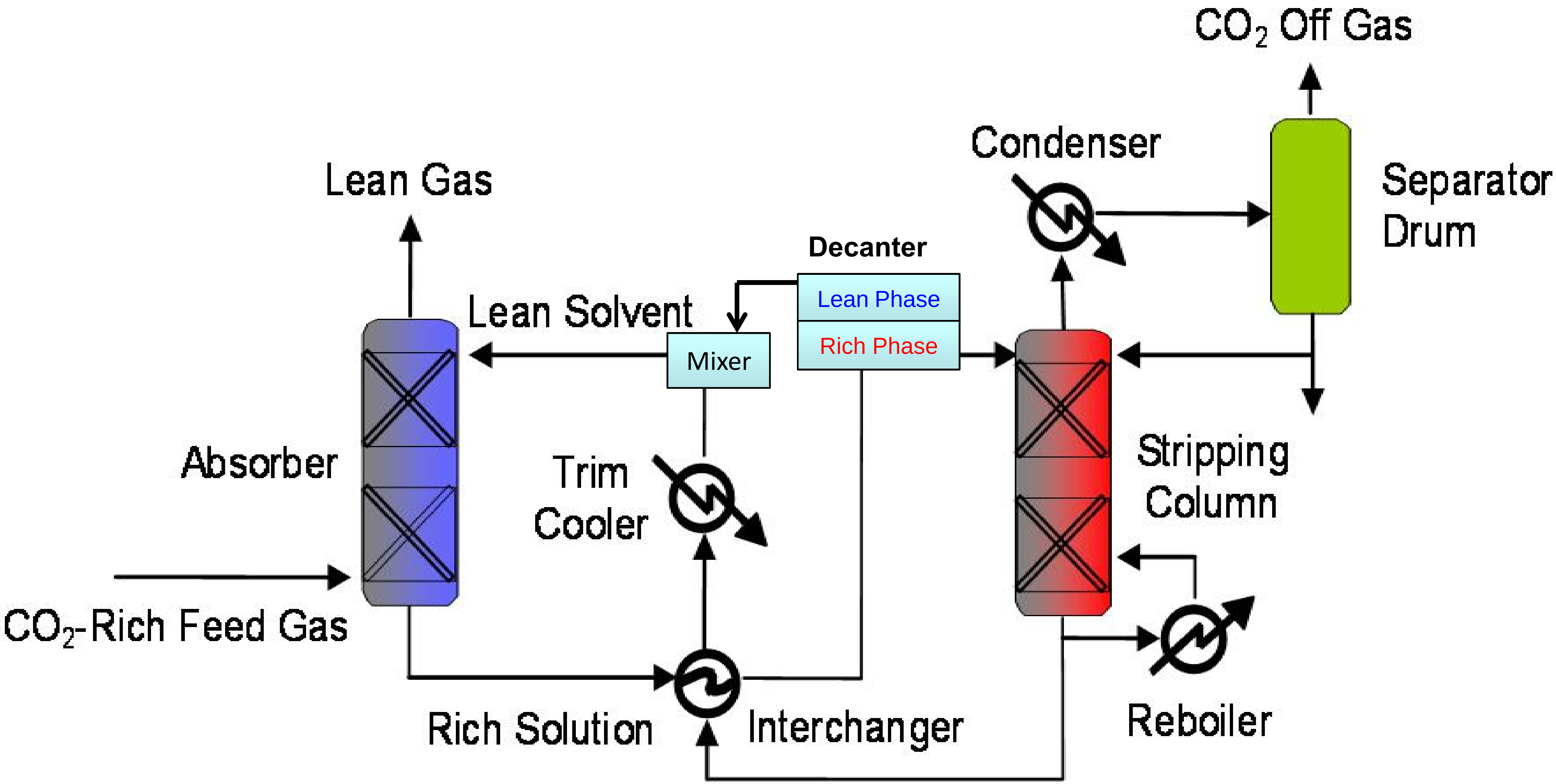
- Phase change solvents has potetial for:

- Low ciculation rate in the desorber
- Smaller size of desorber (low capital cost)
- Improved energy efficiency

Phase change solvent



Introduction



Freezing Point Depression

- Measurement of freezing point is considered the most accurate method to determine water activity
  - Water activity is a key parameter for the amount of water evaporated in the desorber
  - Low water activity means less evaporation of water in the desorber and low energy consumption during solvent regeneration
  - Water activity is only a weak function of temperature
  - Water activity measured at low temperature is not very different from water activity at absorber and stripper temperatures
  - Water activity is very useful for thermodynamic modelling

Experimental: Freezing Point Depression

A, Thermostatic bath with ethanol

B, Cooling jacket

C, Sample glass with magnetic stirrer

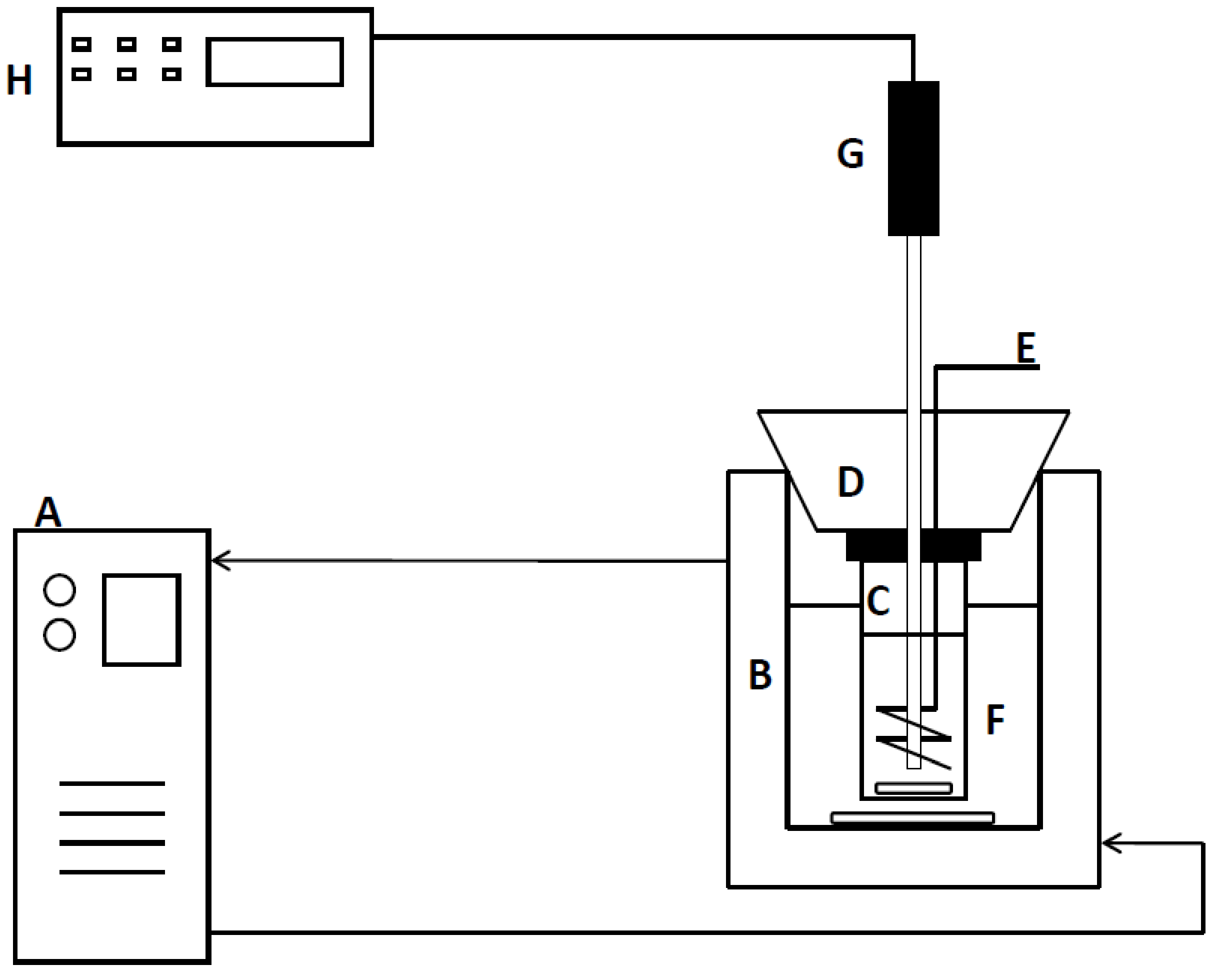
D, Rubber stopper with sample glass lid

E, Device for manual stirring

F, Controlled temperature ethanol bath with magnetic stirrer

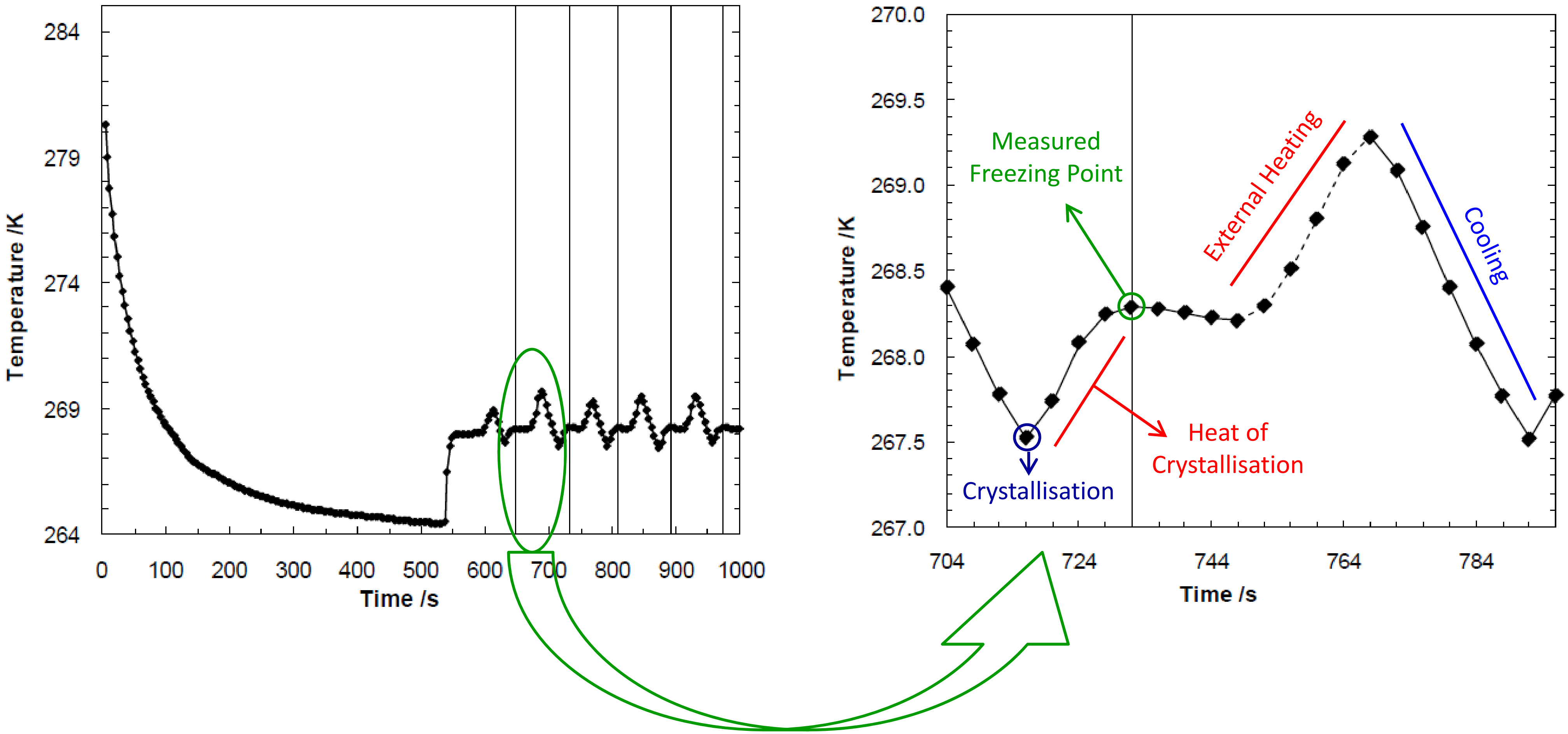
G, Pt100 Thermometer

H, Data acquisition unit



Fosbøl, P. L.; Pedersen, M. G.; Thomsen, K. *J. Chem. Eng. Data* **2011**, 56, 995-1000.

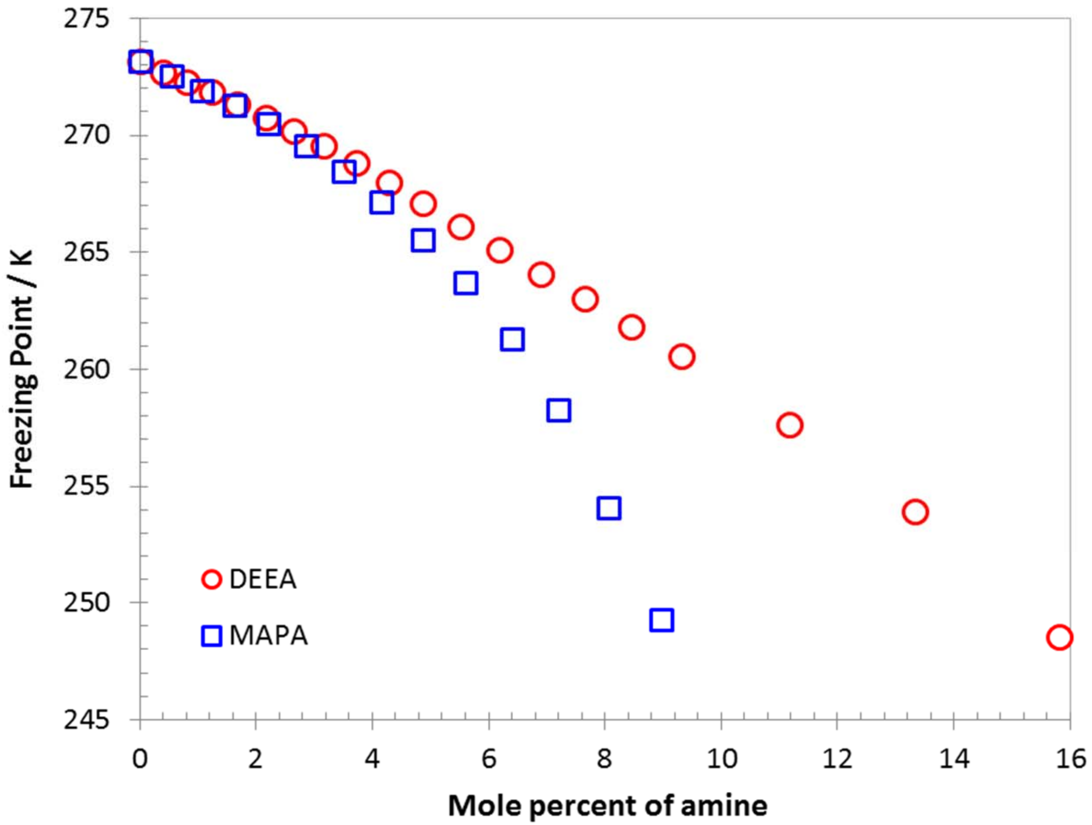
Experimental: Freezing Point Depression



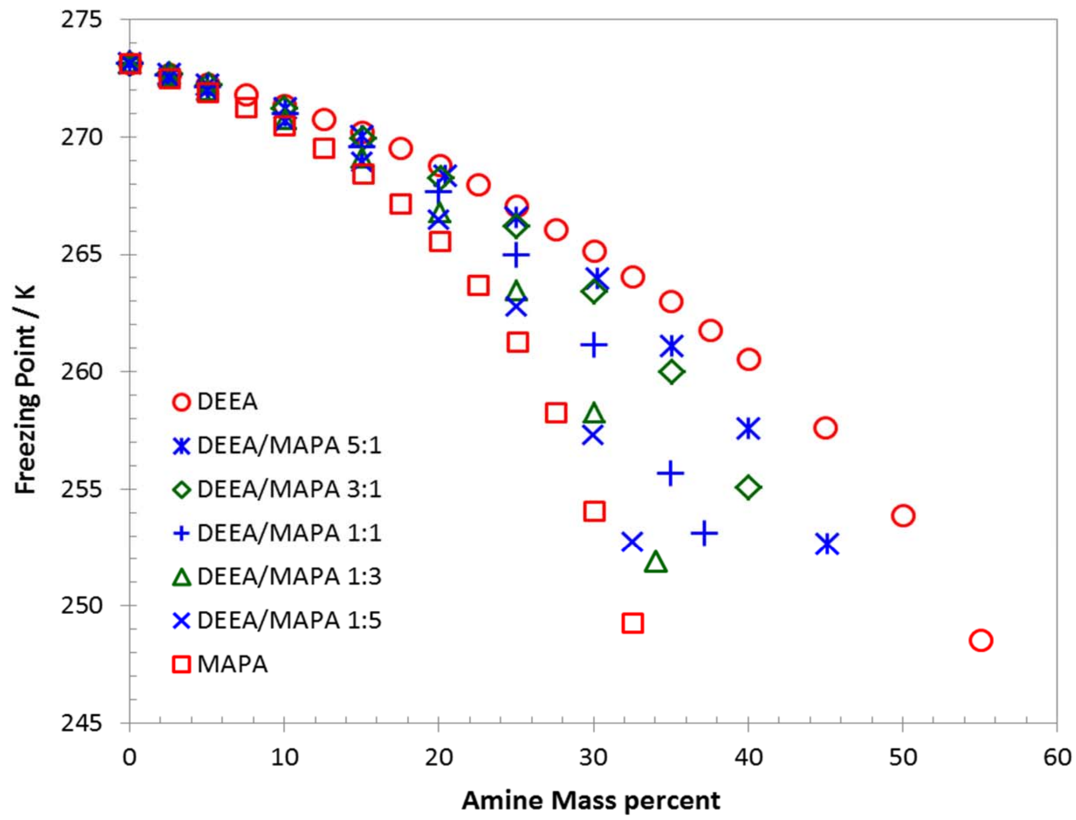
Fosbøl, P. L.; Pedersen, M. G.; Thomsen, K. *J. Chem. Eng. Data* **2011**, 56, 995-1000.

Results: Freezing Point Depression

DEEA-H_2O and MAPA-H_2O



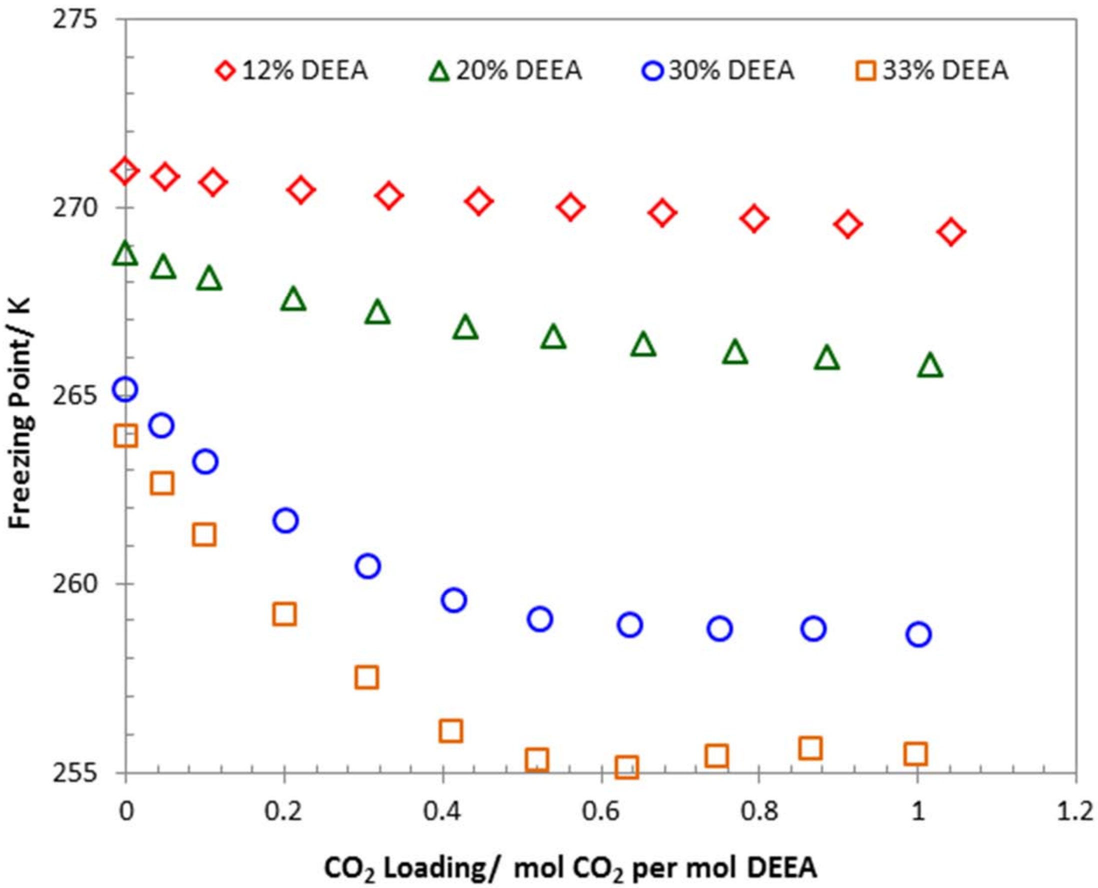
DEEA-MAPA-H_2O



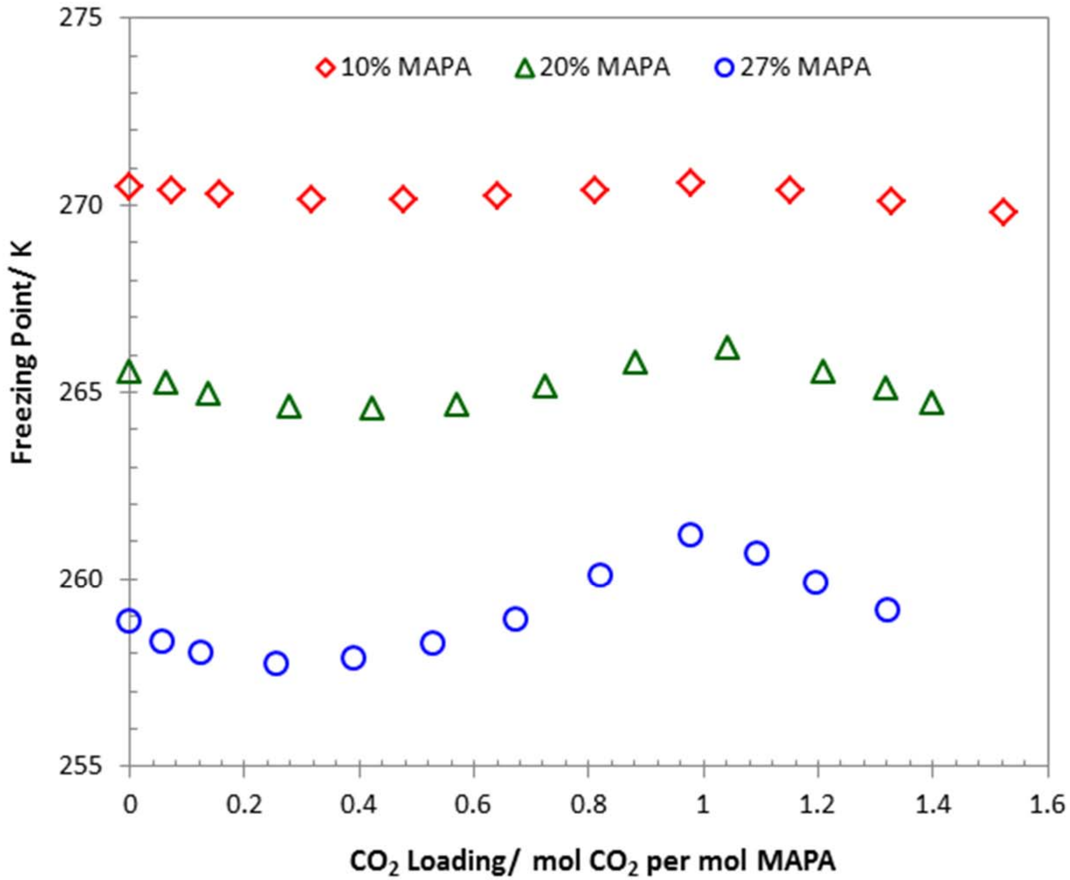
Arshad, M. W.; Fosbøl, P. L.; von Solms, N.; Thomsen, K. *J. Chem. Eng. Data* **2013**, published online.

Results: Freezing Point Depression

DEEA-CO_2-H_2O

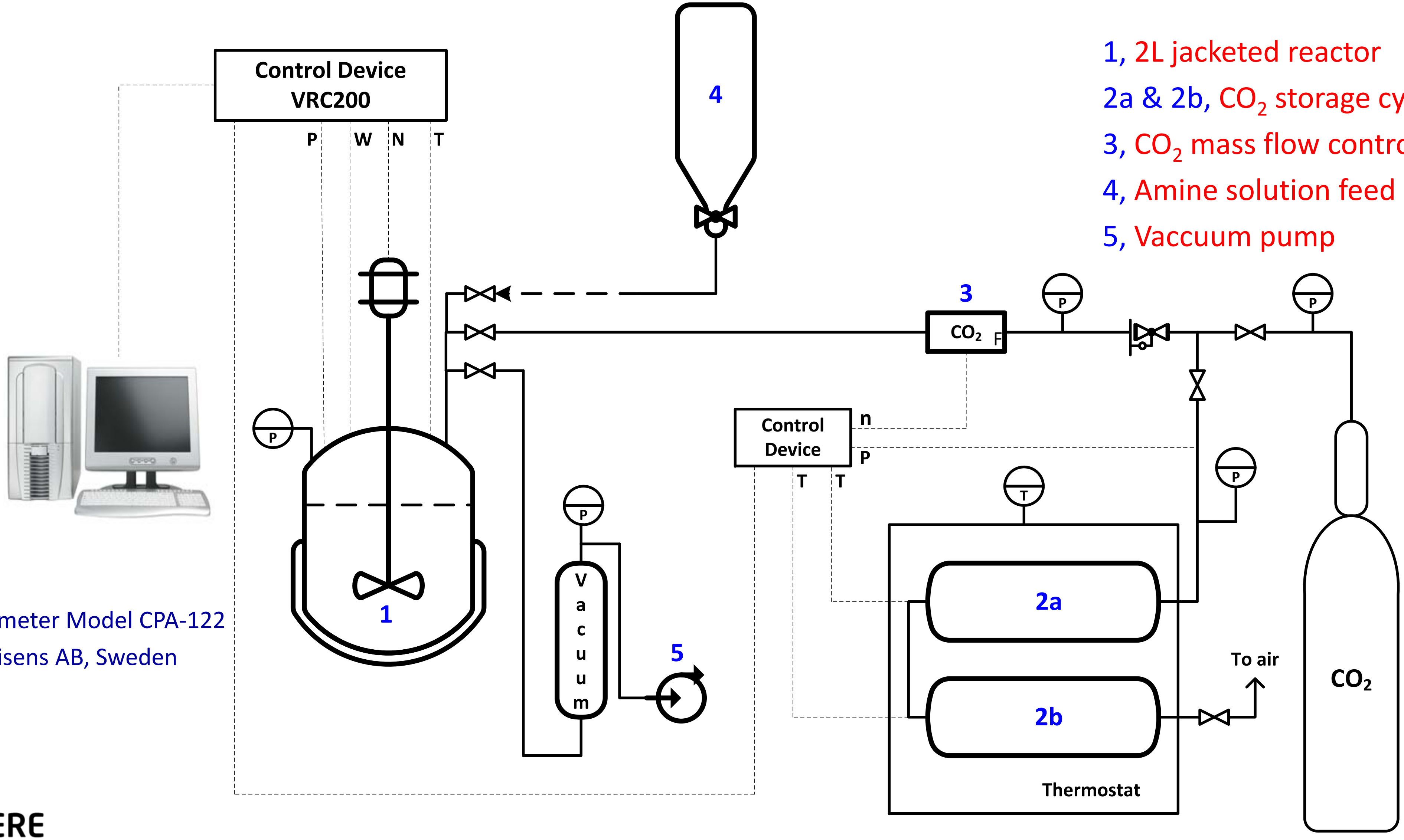


MAPA-CO_2-H_2O



Arshad, M. W.; Fosbøl, P. L.; von Solms, N.; Thomsen, K. *J. Chem. Eng. Data* **2013**, published online.

Experimental: Heat of Absorption and VLE of CO_2



1, 2L jacketed reactor

2a & 2b, CO_2 storage cylinders

3, CO_2 mass flow controller

4, Amine solution feed bottle

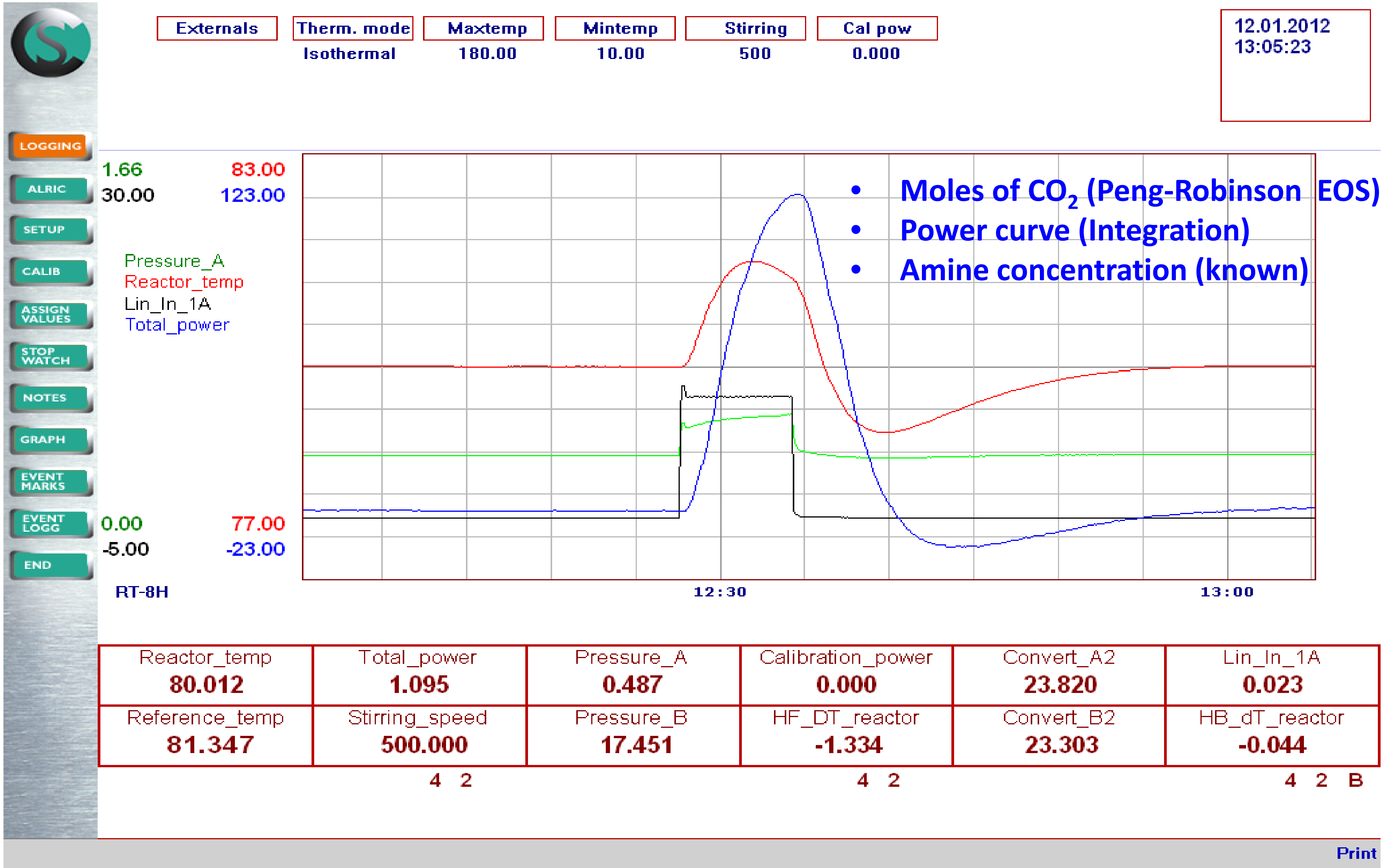
5, Vaccuum pump

Calorimeter Model CPA-122
Chemisens AB, Sweden

Kim, I.; Svendsen. H. F. *Ind. Eng. Chem. Res.* **2007**, 46, 5803-5809

Experimental: Heat of Absorption and VLE of CO_2

- Moles of CO_2 (Peng-Robinson EOS)
- Power curve (Integration)
- Amine concentration (known)



Tested Concentrations

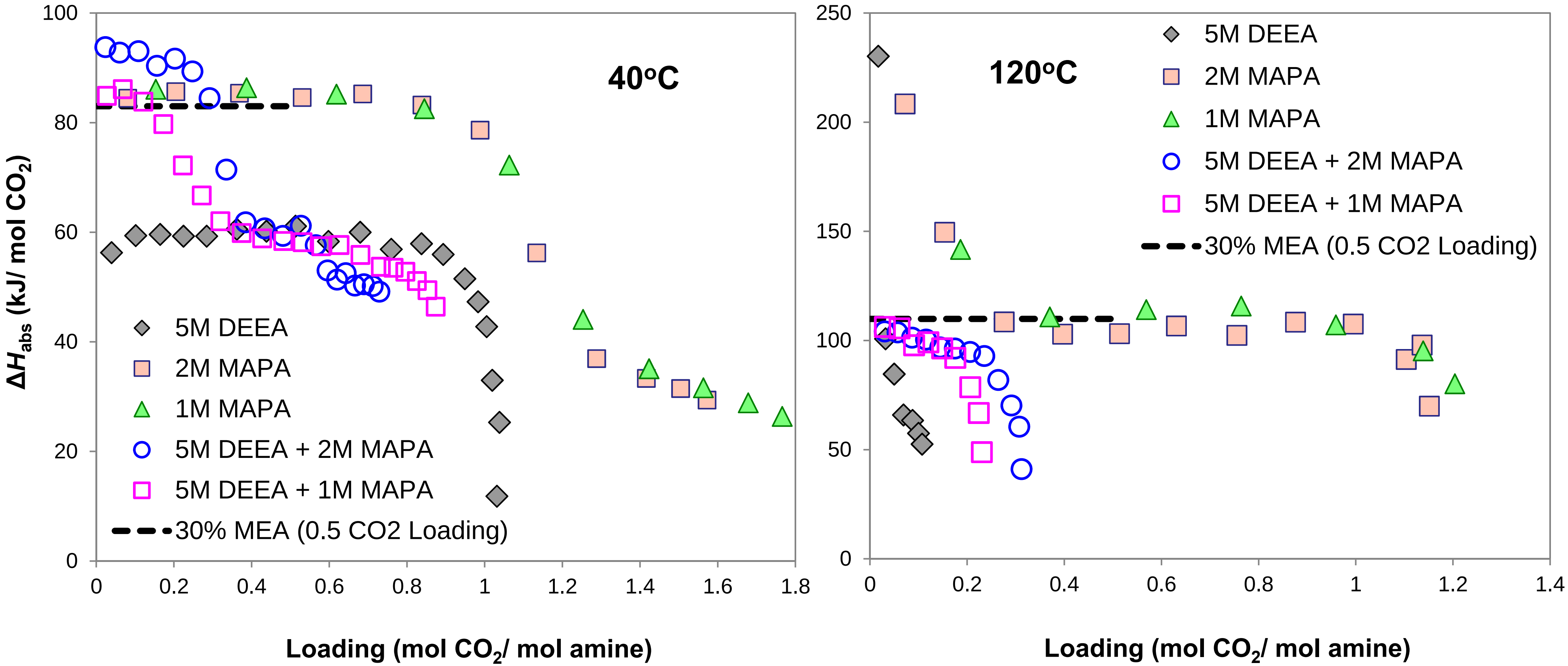
- 5M DEEA
- 2M MAPA
- 1M MAPA
- 5M DEEA + 2M MAPA (phase split)
- 5M DEEA + 1M MAPA (phase split)

Temperature = 40 ^oC (absorption), 80 ^oC and 120 ^oC (desorption)

Total Pressure = ~6 bar

Sample Results: Heat of Absorption

Overall comparison of all systems at Absorption & Desorption conditions

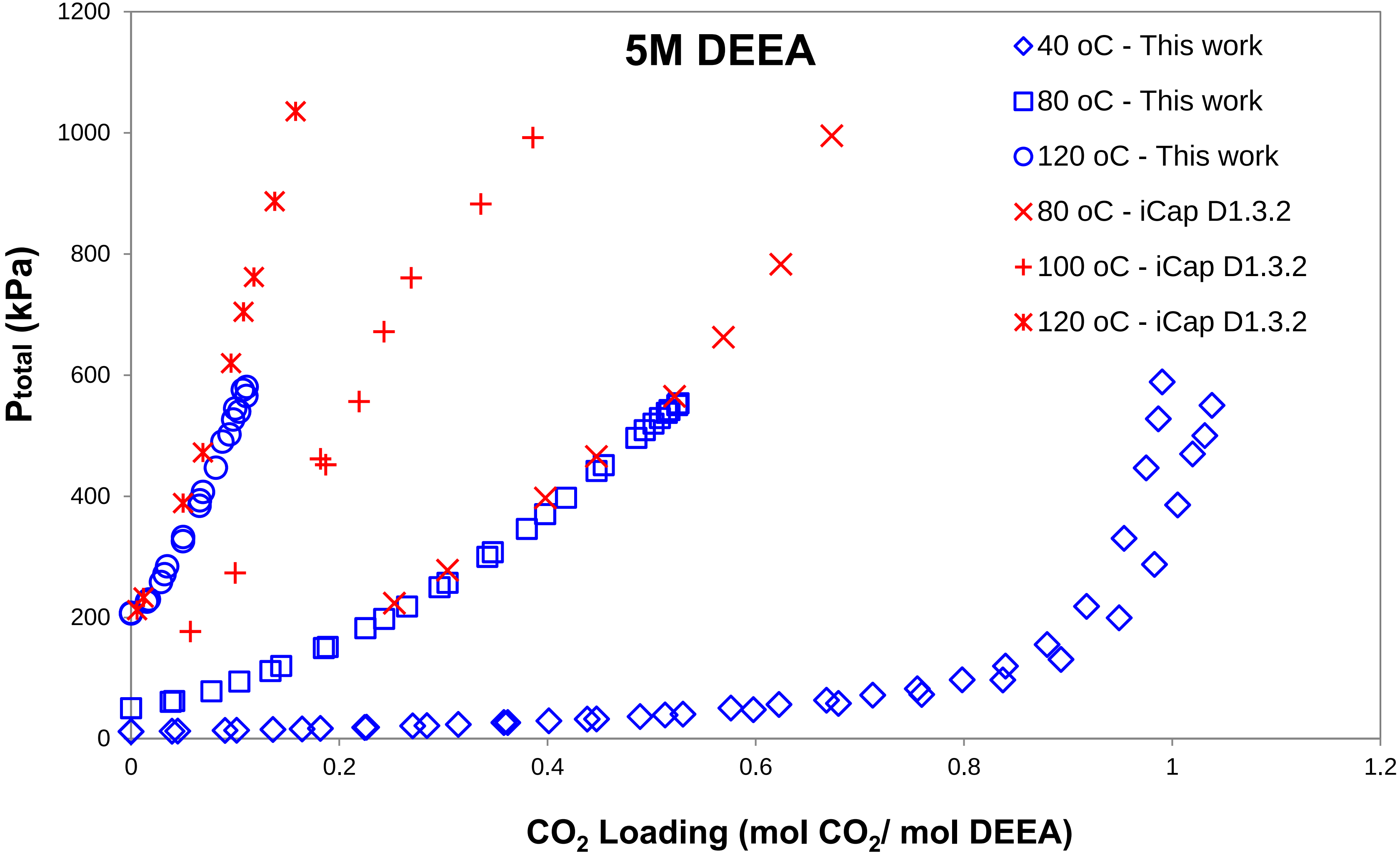


Arshad, M. W.; Fosbøl, P. L.; von Solms, N.; Svendsen, H. F.; Thomsen, K. Submitted to *J. Chem. Eng. Data*.

Sample Results: Vapor-Liquid Equilibrium of CO_2

Blue Data from Calorimeter - This work
Red Data from Equilibrium Cell – iCap D1.3.2

VLE of CO_2 in 5M DEEA



Thermodynamic Modeling

- Amine-CO_2-H_2O systems are electrolyte systems
- Extended UNIQUAC, an electrolyte thermodynamic model will be used to model the phase change solvents system
- The systems to be modeled are:
  - DEEA-CO_2-H_2O
  - MAPA-CO_2-H_2O
  - DEEA-MAPA-CO_2-H_2O (phase split)

Extended UNIQUAC

- Extended UNIQUAC = Original UNIQUAC + Extended Debye-Hückle

$$\frac{G^E}{RT} = \underbrace{\left(\frac{G^E}{RT}\right)_{\text{Combinatorail}} + \left(\frac{G^E}{RT}\right)_{\text{Residual}}} + \left(\frac{G^E}{RT}\right)_{\text{Extended Debye-Hückle}}$$

UNIQUAC entropic term

r = volume parameter

q = surface area parameter

UNIQUAC enthalpic term

Binary interaction energy parameter

$$u_{ij} = u_{ij}^0 + u_{ij}^T\left(T - 298.15\right)$$

Electrostatic interaction

- Liquid phase activity coefficients are calculated with the UNIQAC equation
- Vapor phase fugacity coefficients are calculated with SRK EoS

Modeling: DEEA-CO_2-H_2O

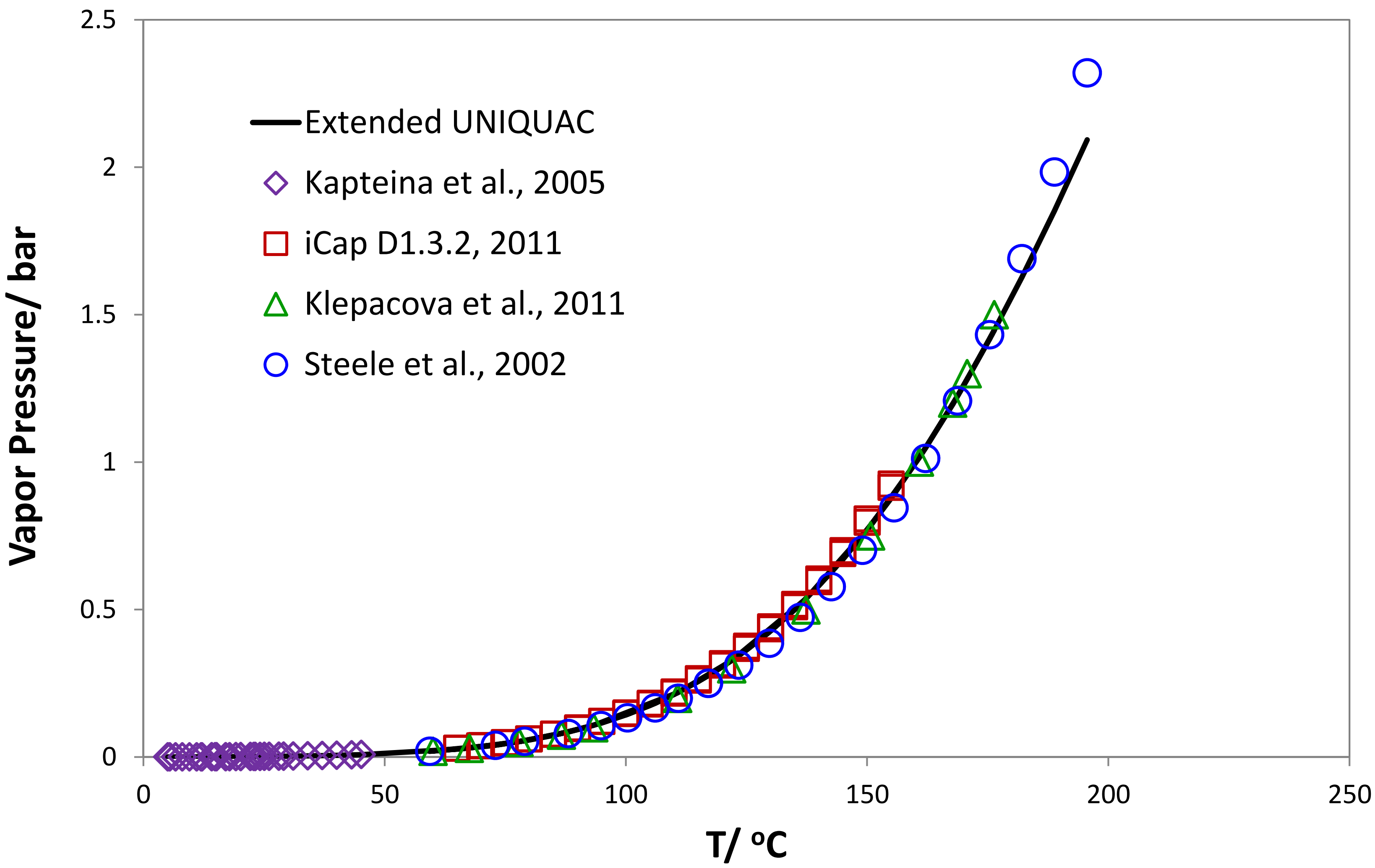
Physical equilibria:

$$CO_2(aq) \leftrightarrow CO_2(g)$$
$$H_2O(l) \leftrightarrow H_2O(g)$$
$$DEEA(aq) \leftrightarrow DEEA(g)$$

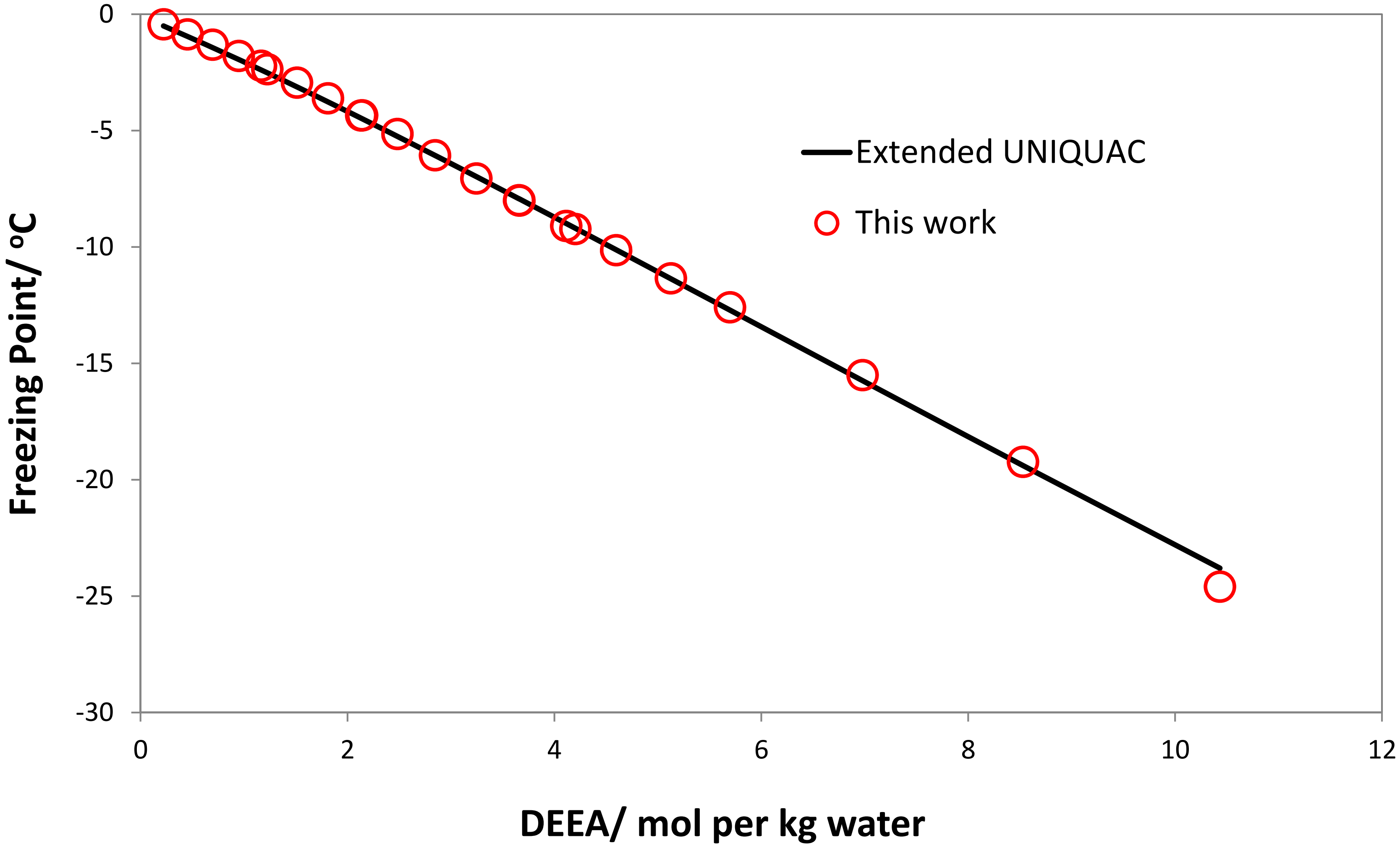
Chemical equilibria:

$$H_2O(l) \leftrightarrow H^+(aq) + HO^-(aq)$$
$$CO_2(aq) + H_2O(l) \leftrightarrow HCO_3^-(aq) + H^+(aq)$$
$$HCO_3^-(aq) \leftrightarrow CO_3^{2-}(aq) + H^+(aq)$$
$$DEEA(aq) + H^+(aq) \leftrightarrow DEEAH^+(aq)$$

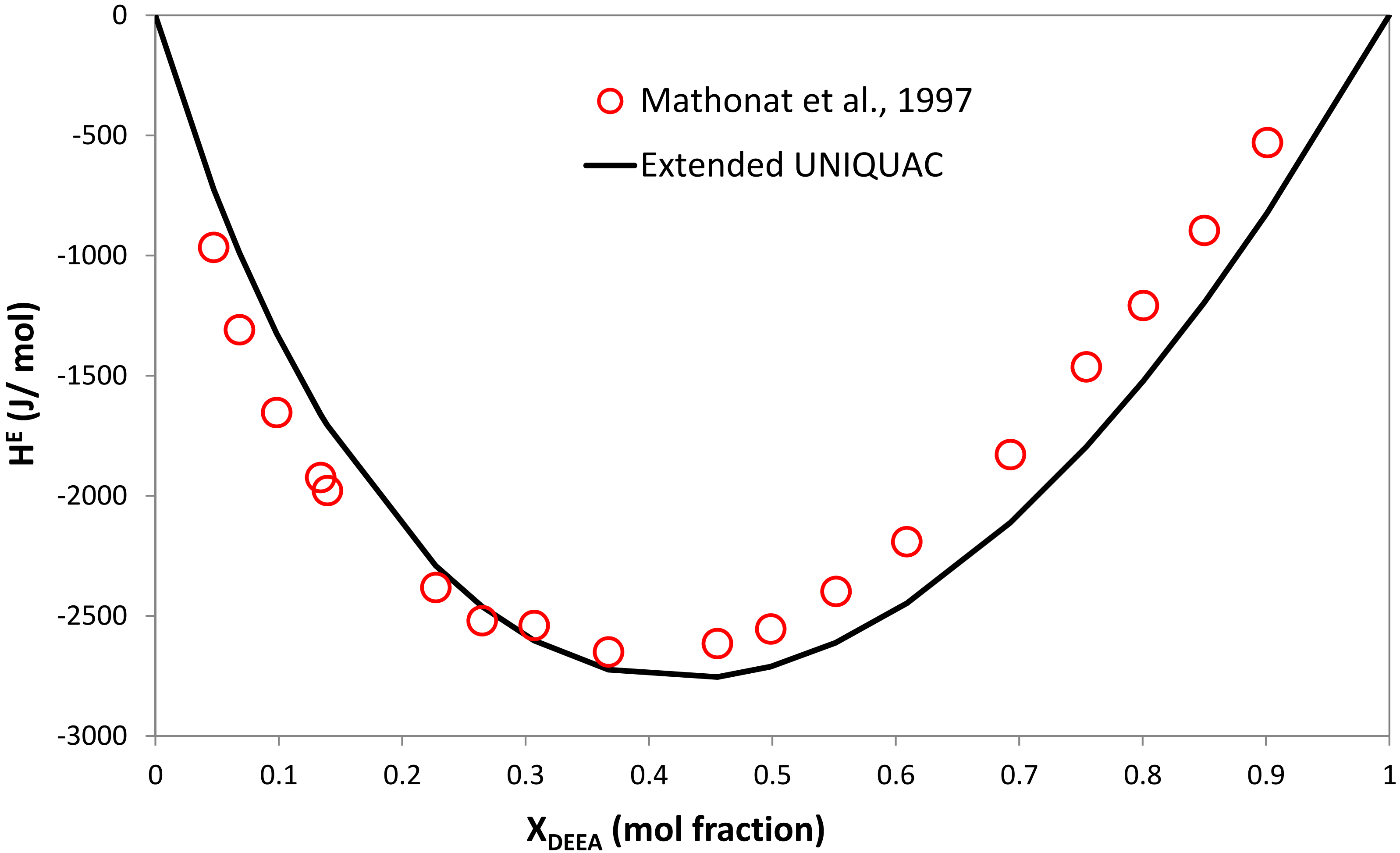
Vapor Pressure of DEEA



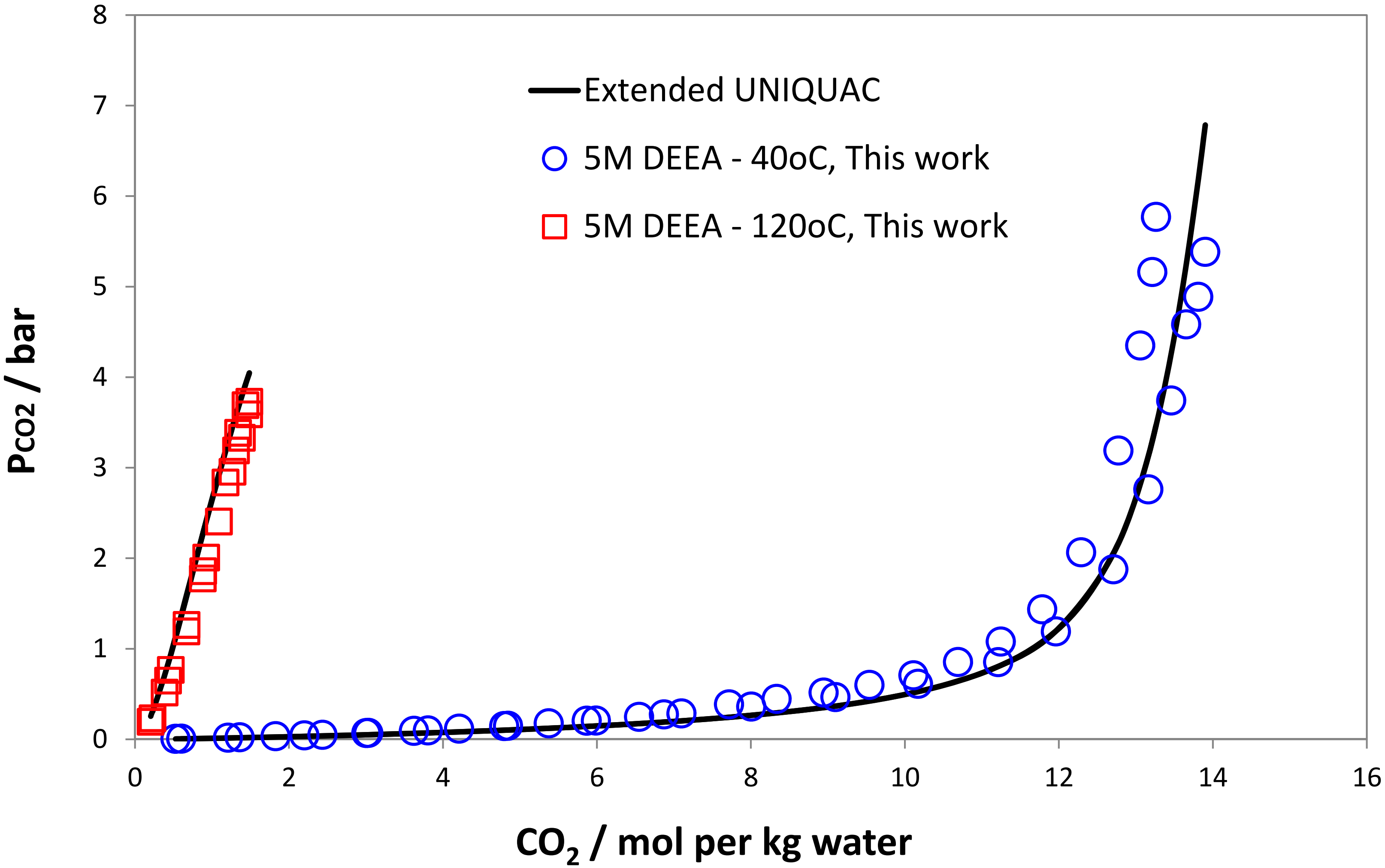
Freezing Point Depression of DEEA



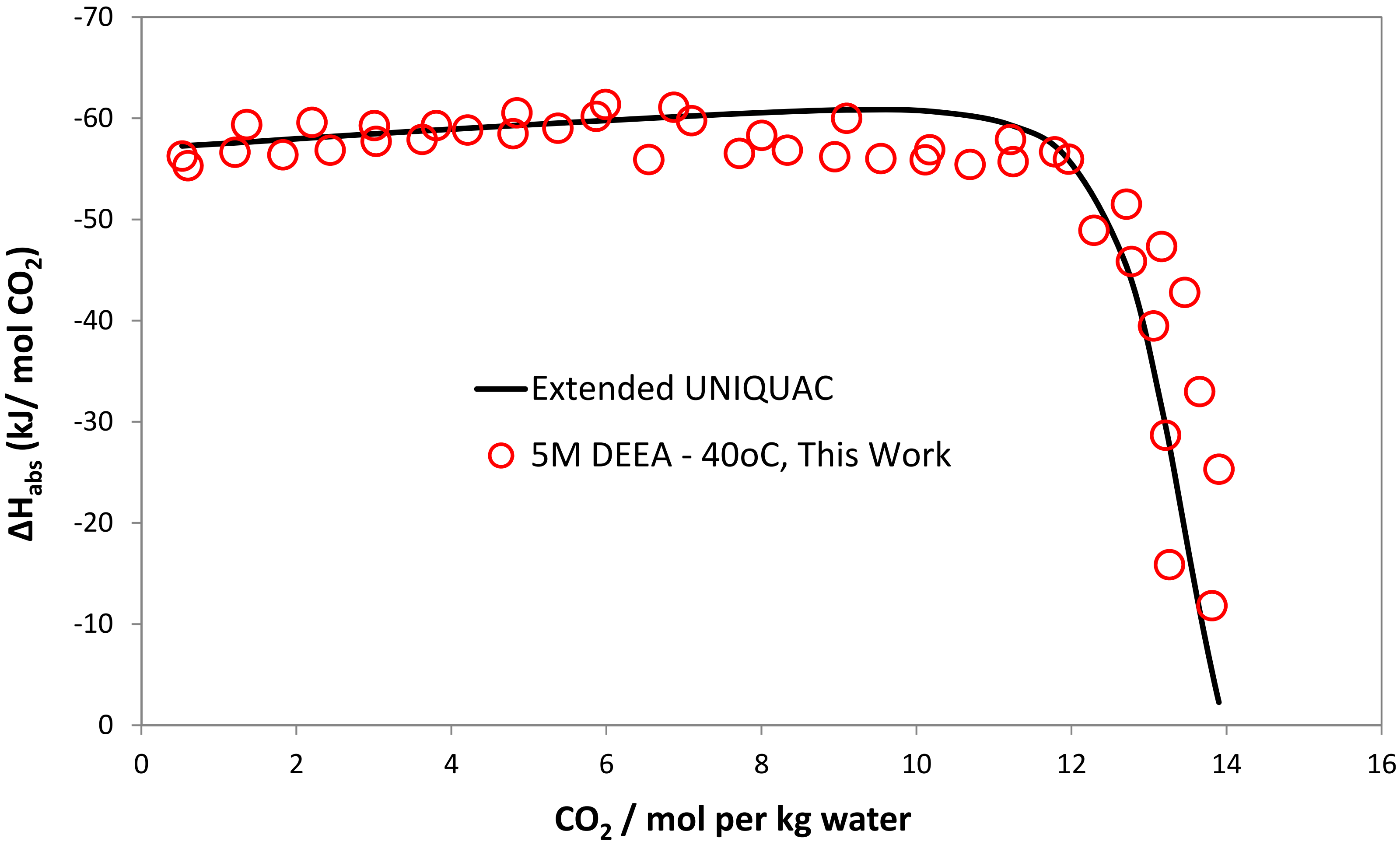
Excess Molar Enthalpy of DEEA



VLE of CO_2 in 5M DEEA



Heat of Absorption of CO_2 in 5M DEEA



Main Conclusions

- Freezing point depressions were measured in CO_2 loaded and unloaded systems
  - Unloaded systems: DEEA-H_2O, MAPA-H_2O and DEEA-MAPA-H_2O
  - Loaded systems: DEEA-CO_2-H_2O and MAPA-CO_2-H_2O
- Heat of absorption and VLE of CO_2 data were measured at 40, 80 and 120^oC for the systems:
  - 5M DEEA and 2M & 1M MAPA
  - 5M DEEA + 2M MAPA (phase split)
  - 5M DEEA + 1M MAPA (phase split)
- Model parameters were determined for the DEEA-CO_2-H_2O system

Future Work

- Improving the model parameters for DEEA-CO_2-H_2O system
- Modeling the MAPA-CO_2-H_2O and DEEA-MAPA-CO_2-H_2O systems

Acknowledgement

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SEVENTH FRAMEWORK PROGRAMME

Thank You!